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Title:	Exploring Interactions among Nanocrystals with Multidimensional Nanoscopy
Author(s):	Ryan, Duncan Patrick
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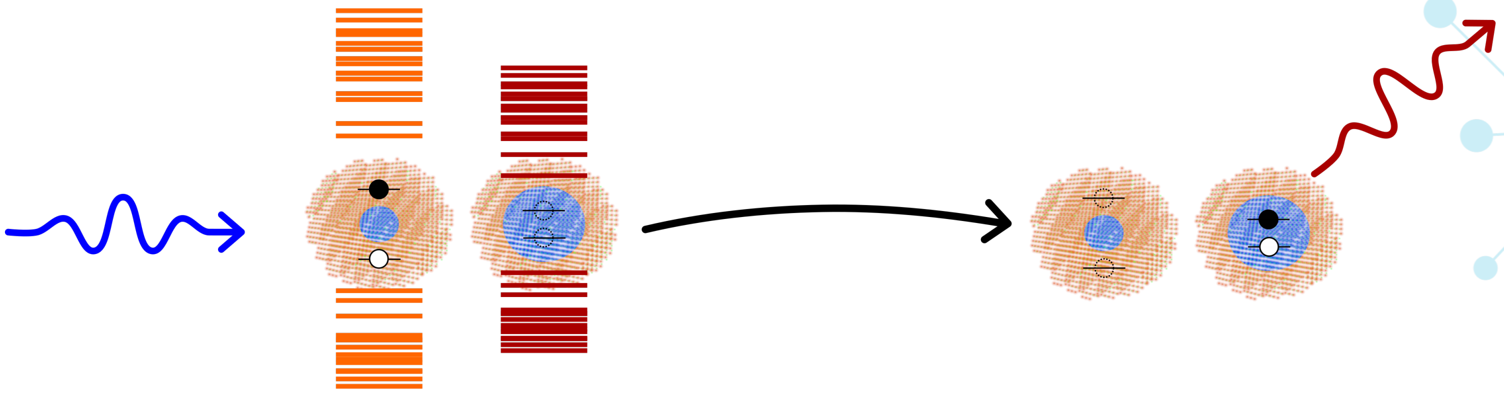
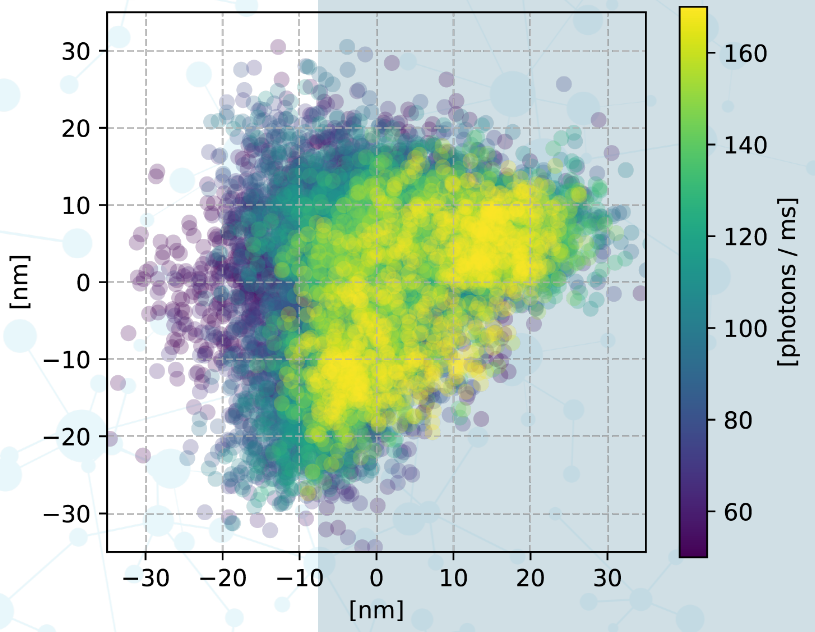
Exploring Interactions among Nanocrystals with Multidimensional Nanoscopy



Duncan P Ryan, Los Alamos National Laboratory



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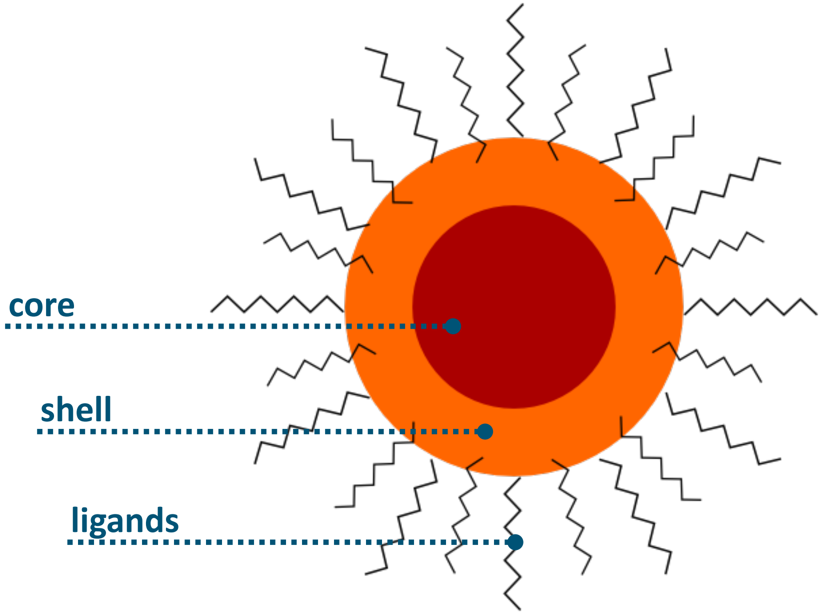
Quantum Dot Nanocrystals

Fluorescent Particles

2 – 10 nm diameter
Tunable emission in optical region
High quantum yield (bright)

Halber, *Spectrum* (2011)

Structural components:

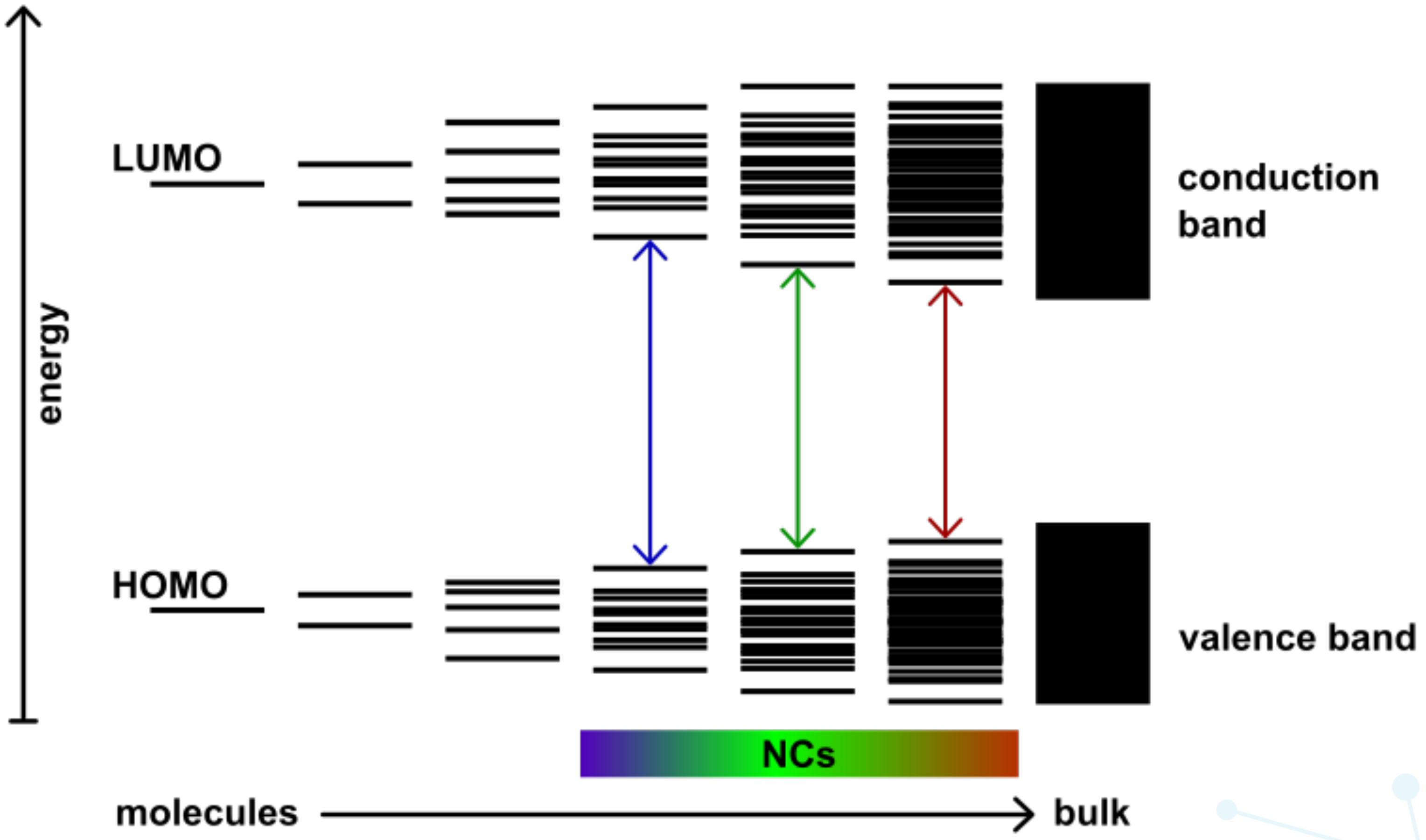


Core/shell are semiconductor material (ex. CdSe/ZnS), define basic emission properties through intrinsic bulk material bandgap.

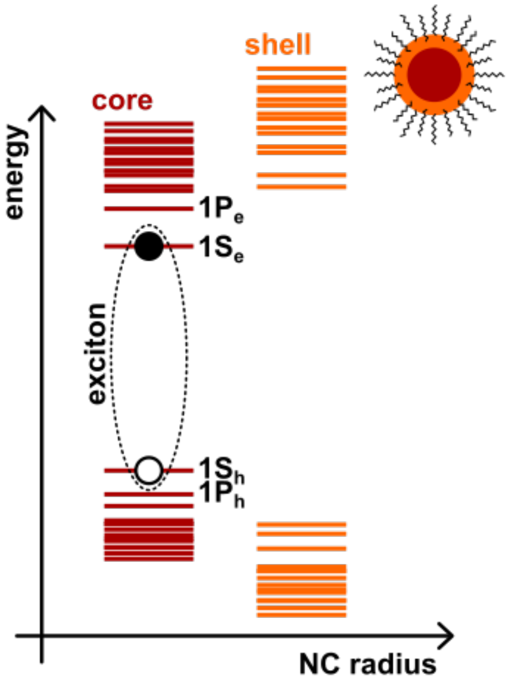
Ligands protect and stabilize NCs from environment.

Quantum Dot Nanocrystals

The structure of NCs energy levels are the result of quantum confinement.



Quantum Dot Spectral Properties



An **exciton** is the combined pair of an electron and hole.

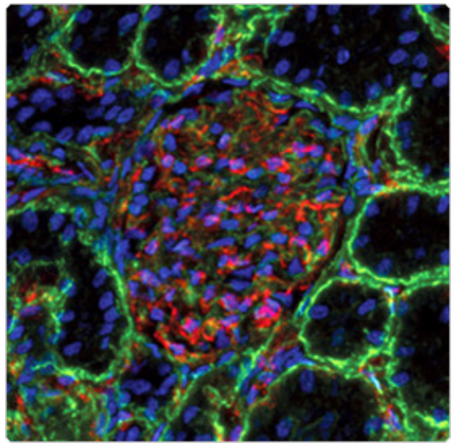
Shells confine excitons to core of the nanoparticle.

Quantum Dot Nanocrystals

Displays

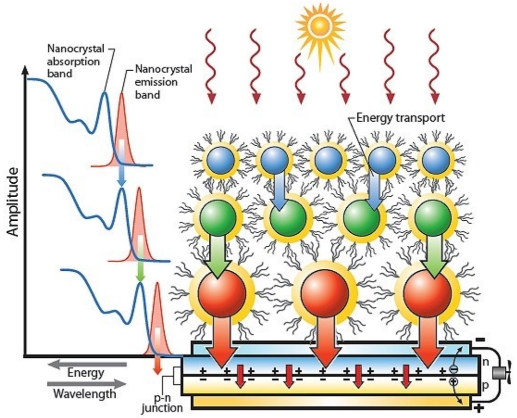
Campbell, *Apple Insider* (2014)

Research & Imaging

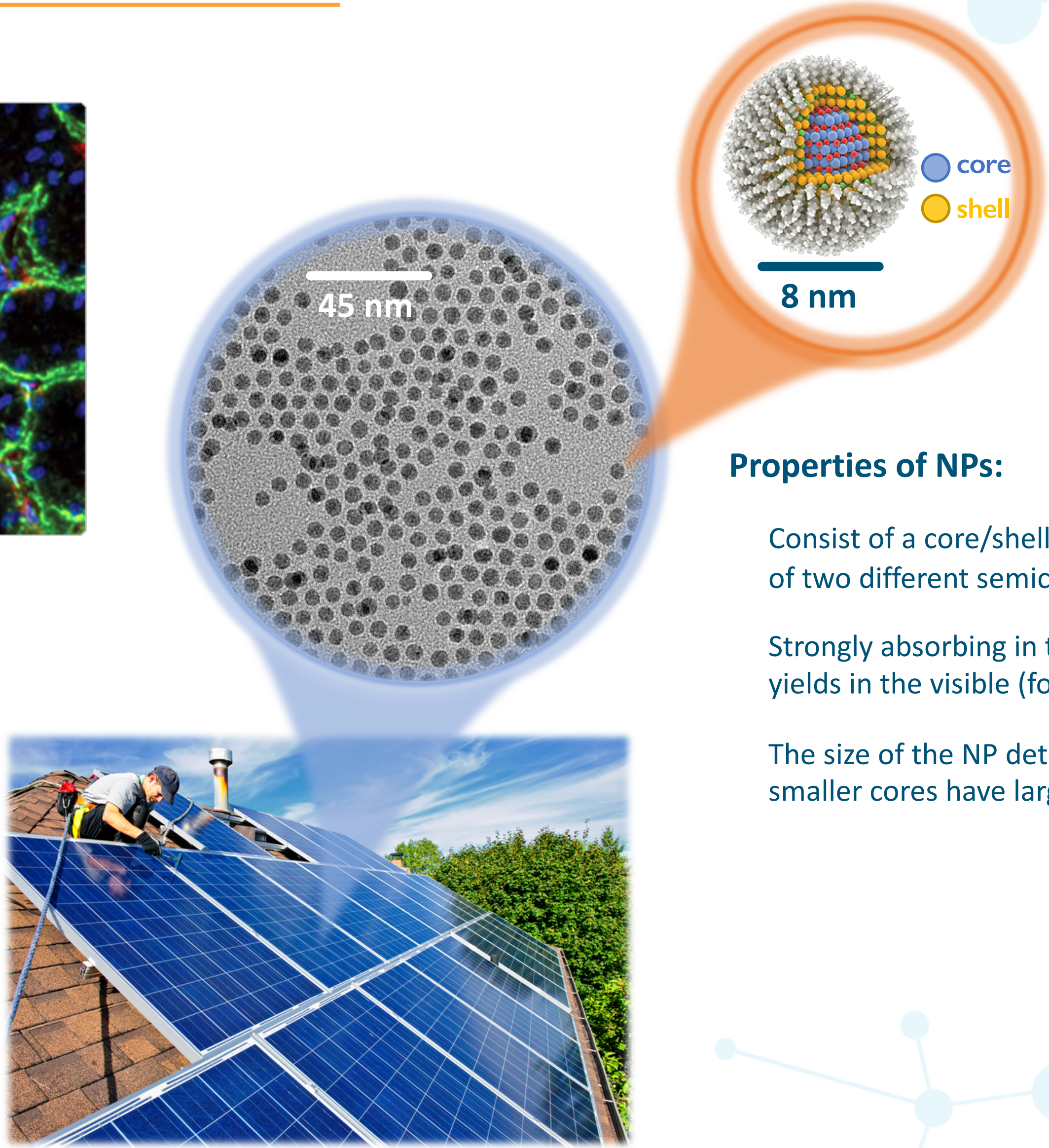


Life Technologies

Photovoltaics & Solar



Los Alamos Science & Tech Magazine



Properties of NPs:

Consist of a core/shell structure, often made up of two different semiconductor materials.

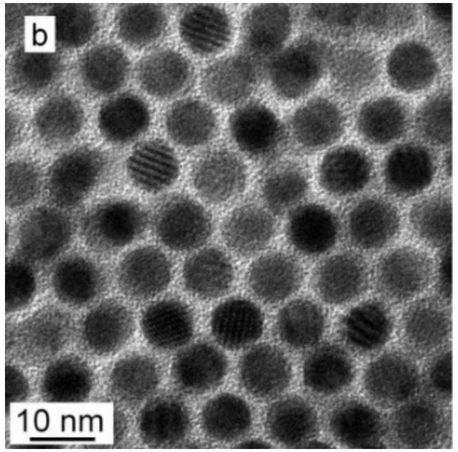
Strongly absorbing in the UV and high quantum yields in the visible (for a CdSe system).

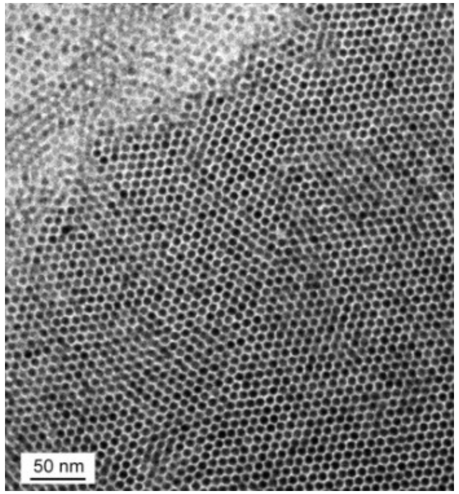
The size of the NP determines the energy levels: smaller cores have larger bandgaps.

Networks of Nanoparticles

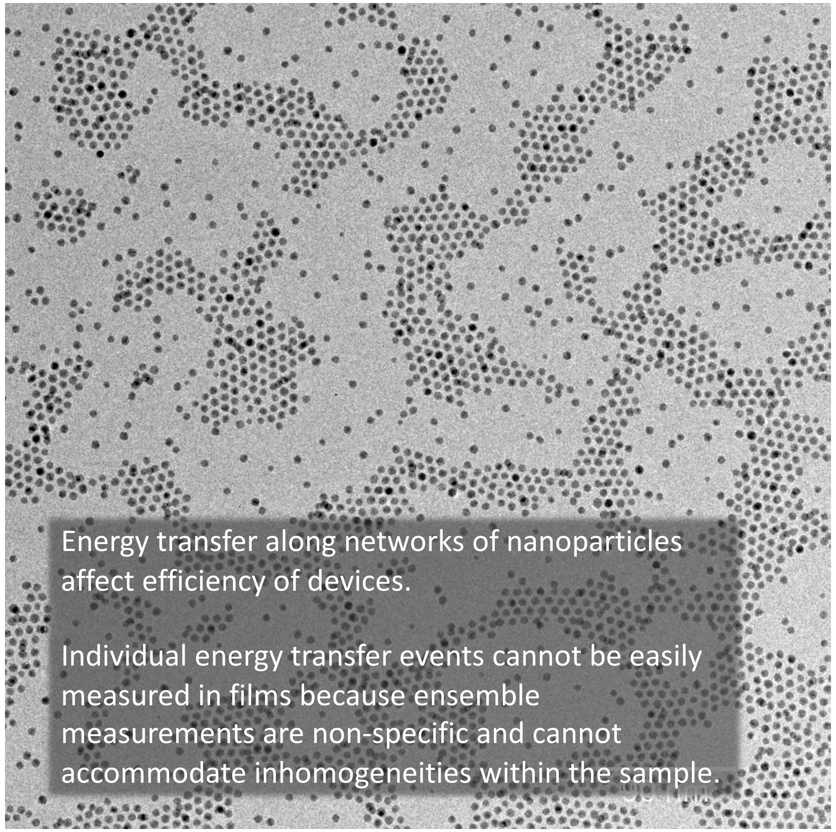
Films → **Networks** → **Neighbors**

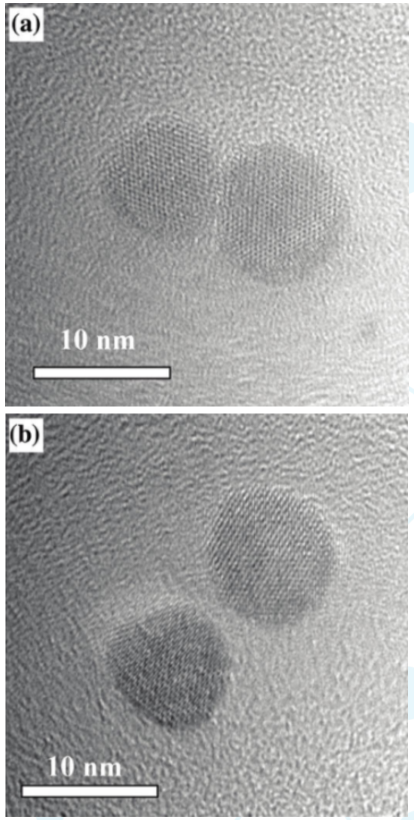
Small clusters of NPs are a model system to study interactions with single-molecule techniques.





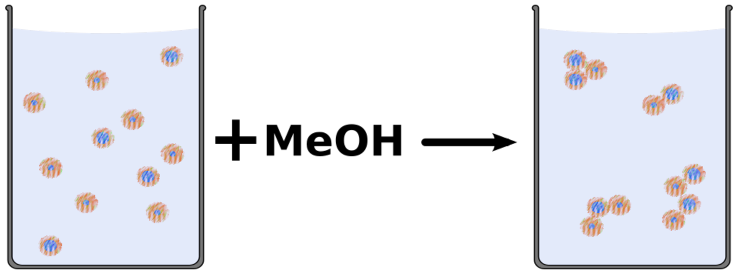
Talapin, *Nano Letters* (2007)





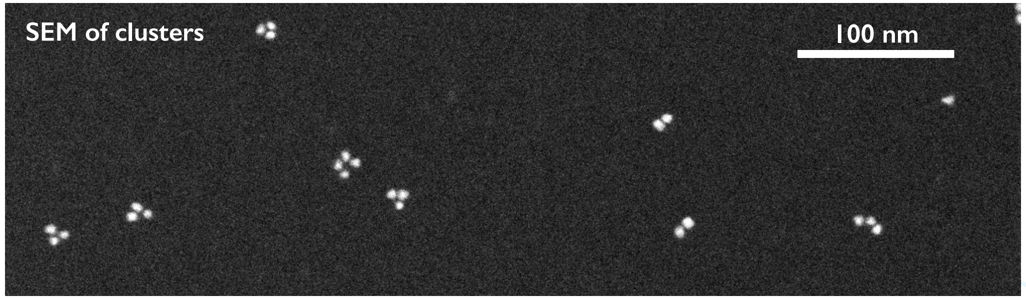
Xu, *JACS* (2011)

Fluorescence from Interacting NP Clusters



Clusters are formed by slowly stripping ligands in solution to form surface-to-surface attachment.

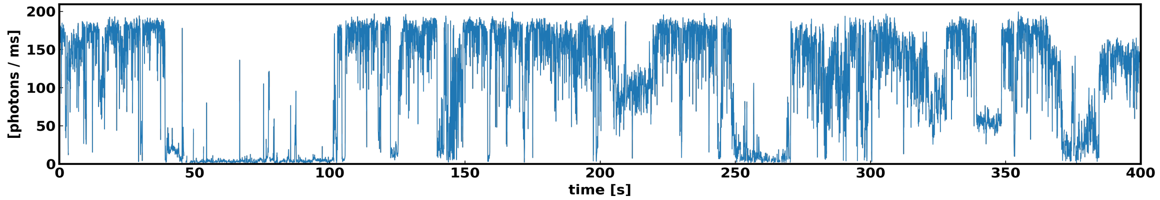
CdSe/CdS or **CdSe/ZnS** semiconductor NPs



A distribution of cluster sizes and geometries are produced

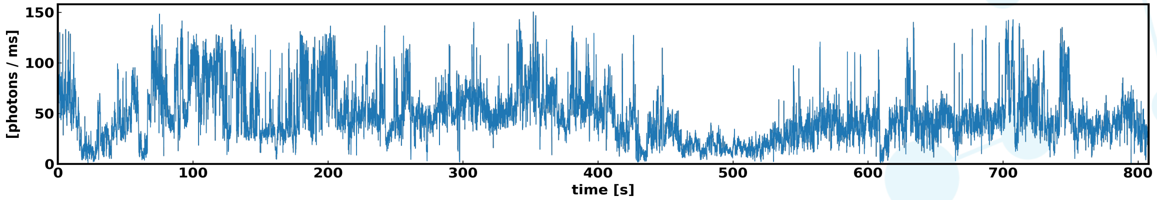
Emission fluctuations: blinking

Single NP



Individual NPs exhibit **binary** or **telegraph** blinking

NP cluster

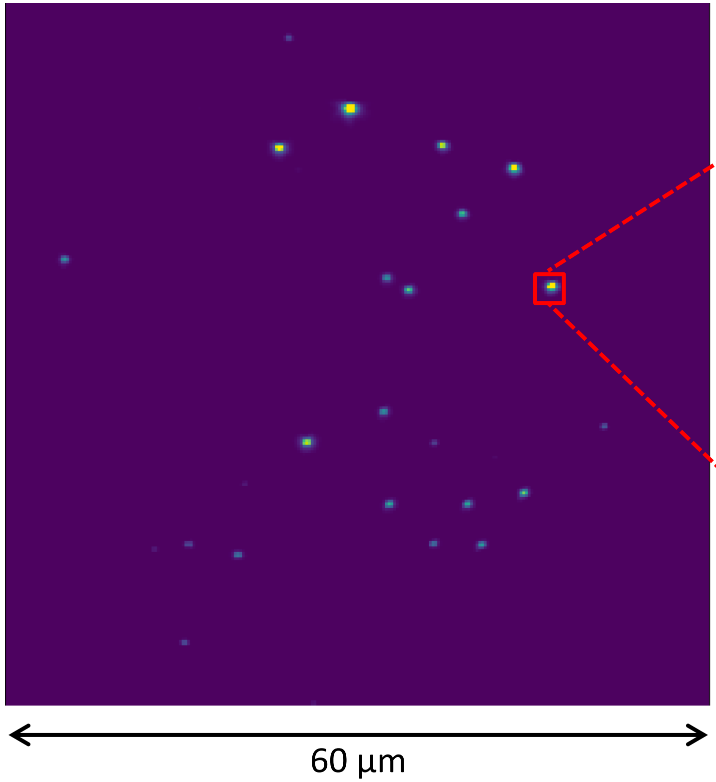


Clusters of NPs will interact, resulting in **enhanced** blinking with rapid intensity modulations that typically lack discrete intensity levels.

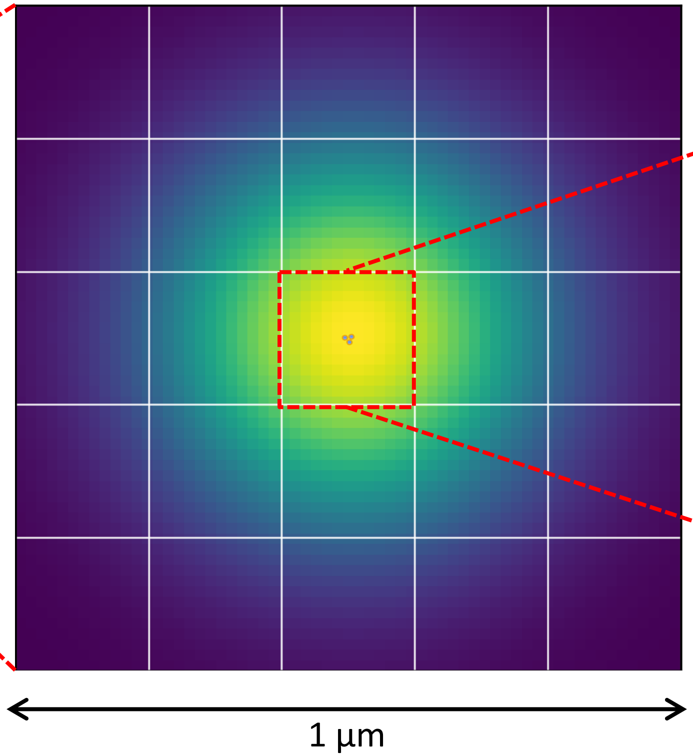
Optical Super-resolution Imaging of NP Clusters

Where in a NP cluster is the emission coming from?
To study collective fluorescence behaviors in NP clusters, turn to super-resolution imaging.

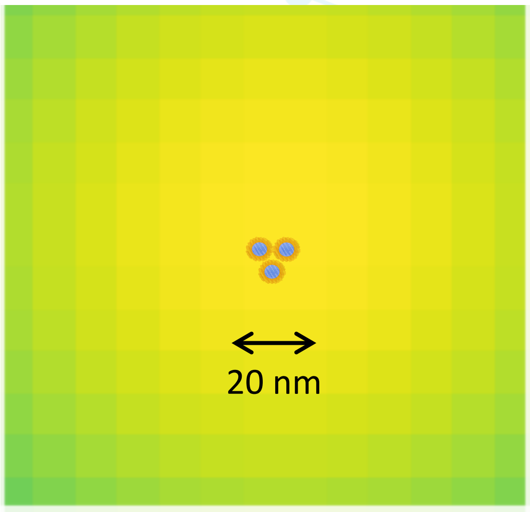
Camera field of view



Point spread function of NP cluster



NP cluster size compared to size of a single camera pixel



NP clusters are smaller than the diffraction-limit of their fluorescence: ~8nm.
Resolving individual NPs in a cluster requires nanometer resolution.

Super-resolution Microscopy

Particles can be resolved below the diffraction-limit of visible light. From 250 µm to 5 nm.

Super-resolution microscopy is a collection of techniques:

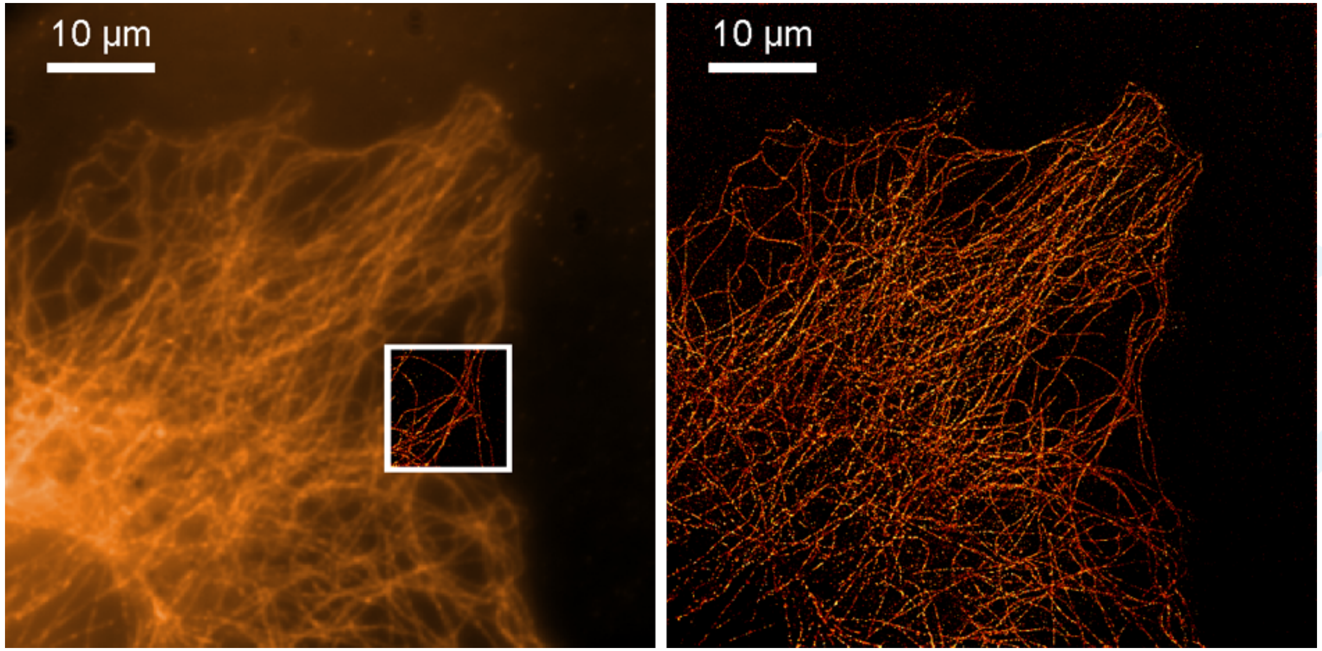
- Fluorescent probe physics/dynamics
- Instrumentation
- Analysis algorithms

Many super-resolution methods are **single-particle** approaches: particles are examined individually

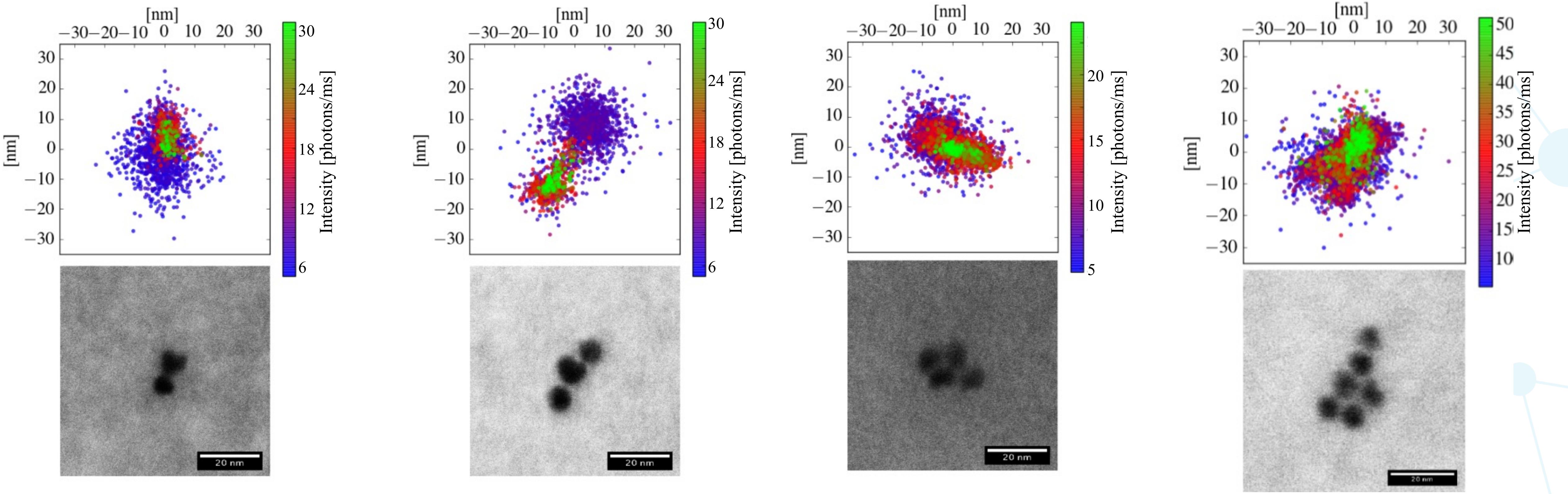
Super-resolution microscopy earned the 2014 Nobel Prize in Chemistry for Eric Betzig, Stefan Hell, and William Moerner.

Wide-field image

Super-resolution image (dSTORM)



Super-resolution Imaging of NP Clusters

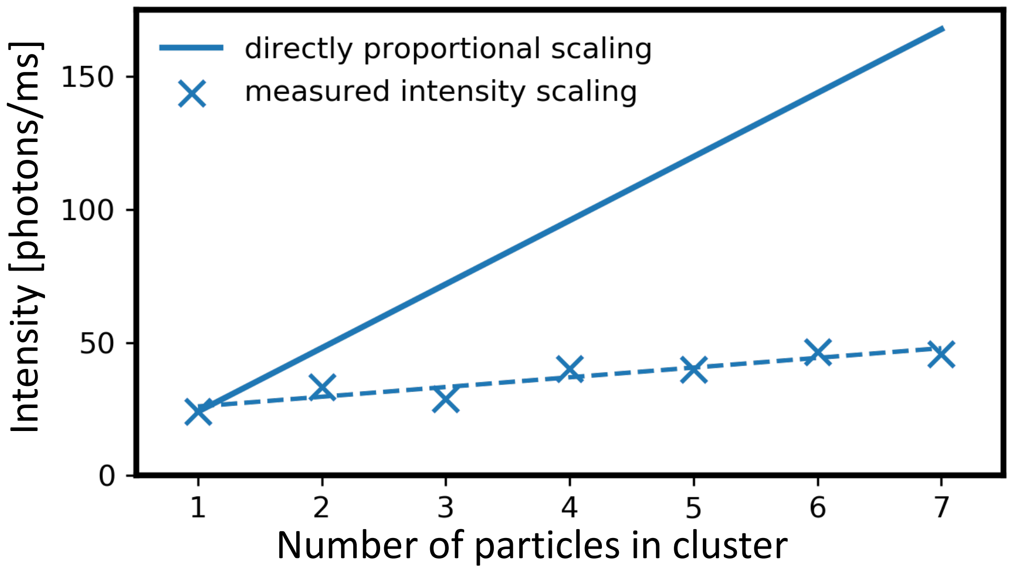


Correlated fluorescence super-resolution and SEM imaging compared implied cluster geometry with the true geometry.

“Hot-spots” emerge as dominant emission regions within NP clusters

Ryan, D. P. *et al.* Quantum dot clusters visualized by polarization- and wavelength-resolved nanoscopy. *In prep*.

Correlation with Cluster Size

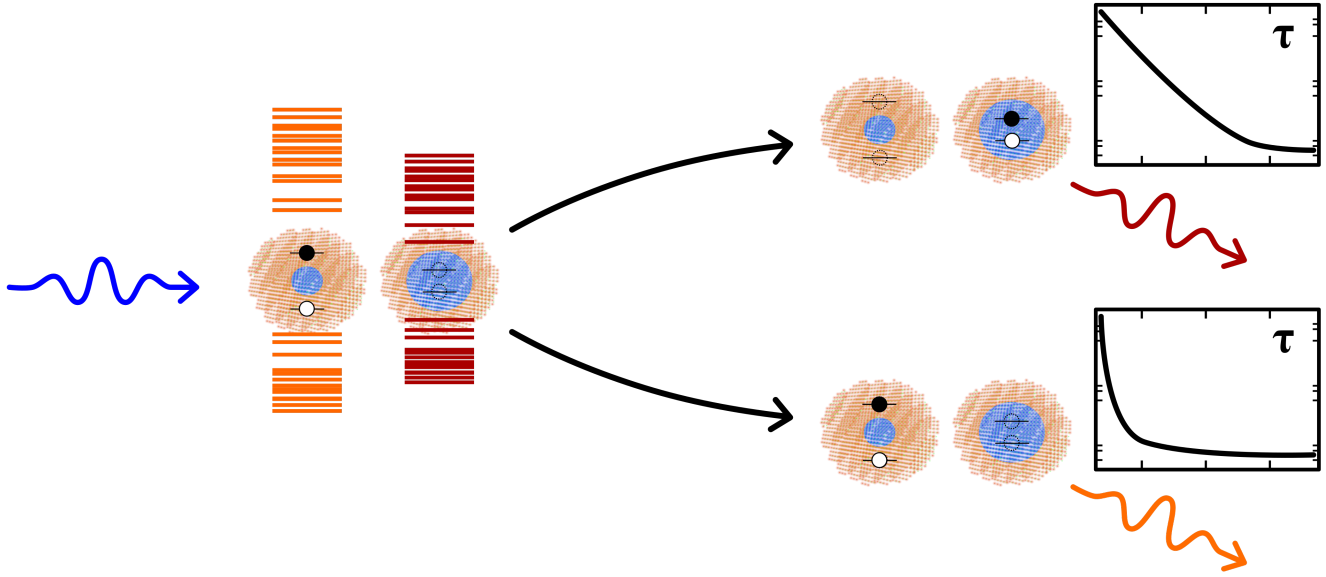


Total cluster emission intensity does not scale simply with cluster size. Additional NPs do not increase emission as significantly as independent NPs.

Exciton loss mechanisms suppress emission intensity.

Ryan, D. P. *et al.* “Mapping Emission from Clusters of CdSe/ZnS Nanoparticles.” *J. Phys. Chem. C* **122**, 4046–4053 (2018).

Energy Transfer



Model for energy transfer:

An excited donor can (a) emit a photon or (b) transfer the exciton to a nearby acceptor.

Because fluorescence and energy transfer are competing processes, the direct donor emission will appear quenched with a shorter lifetime and at a lower intensity.

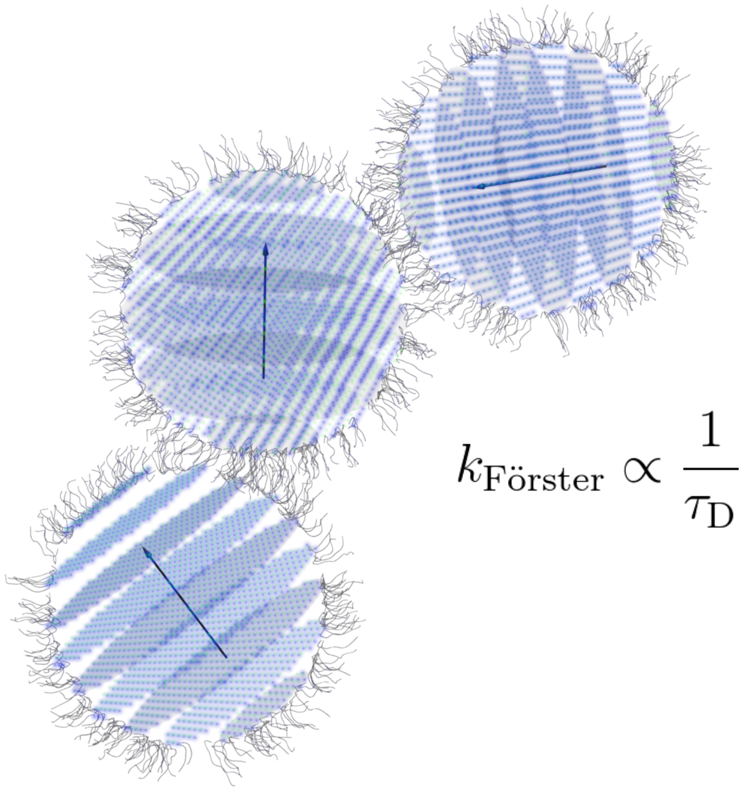
Emission from an acceptor will be enhanced due to the additional excitons funneled through energy transfer and will have the intrinsic lifetime of an individual NP.

Energy transfer has signatures in:

- Intensity (enhanced blinking)
- Spatial (emission center moves)
- Lifetime
- Spectral
- Orientation

Combining localization information with lifetime information can reveal dynamics and relationships among energy transferring NPs.

Orientation Components of Energy Transfer

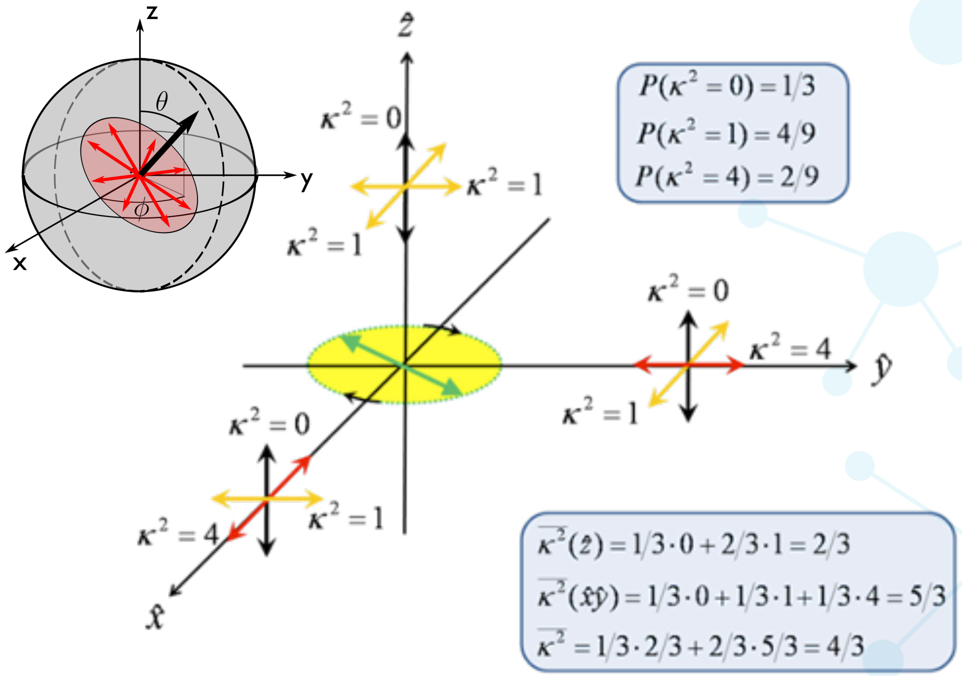


orientation factor

$$k_{\text{Förster}} \propto \frac{1}{\tau_{\mathrm{D}}} \frac{\kappa^2}{r^6} \int \underbrace{\mathrm{d}\lambda\, \lambda^4 f_{\mathrm{D}}(\lambda)\, \epsilon_{\mathrm{A}}(\lambda)}_{\text{spectral overlap}}$$

particle separation

NPs emit from a 2D dipole



Bene, L.; Bagdány, M.; Damjanovich, L. "Checkpoint for Helicity Conservation in Fluorescence at the Nanoscale: Energy and Helicity Transfer (HFRET) from a Rotating Donor Dipole." Biophysical Chemistry 2018, 239, 38–53.

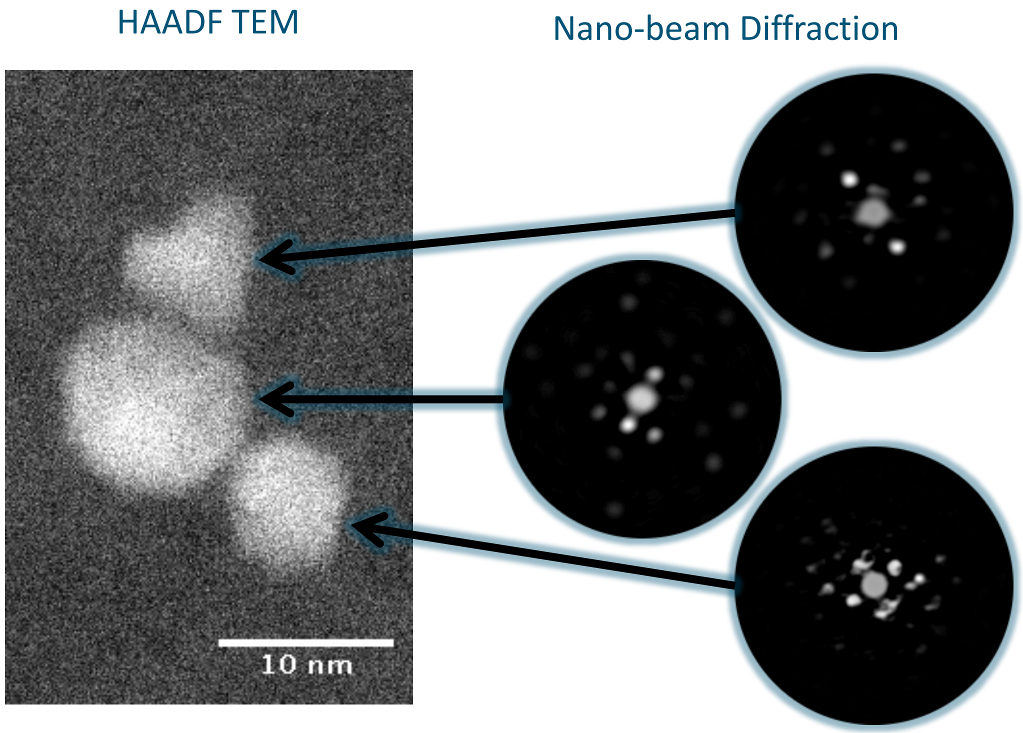
Orientation factor κ^2 strongly dictates coupling efficiency in FRET.

Other coupling strength parameters: spectral overlap and separation distance

As 2D emitters, NPs require additional considerations to determine κ^2.

In fixed nanostructures, using the typical averaged κ^2 value is not appropriate.

Orientation Mapping of NP Clusters



Different orientations from diffraction patterns.

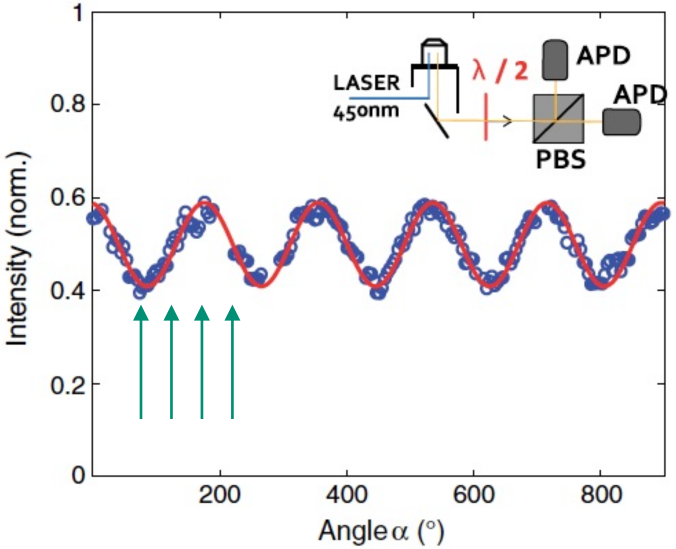
Irregular shapes and shell thicknesses from contrast imaging. Not ideal NPs for energy transfer studies.

Never use commercial NPs: reviewers will hate it.

Polarization Imaging for Orientation Measurement

Conventional confocal setup (continuous monitoring)

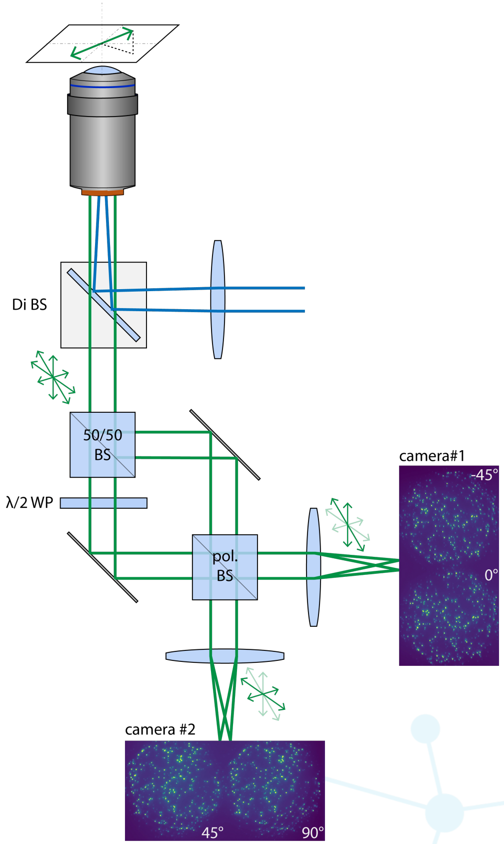
- Established method for non-imaging based polarization and orientation measurements.
- Low throughput
- Does not super-resolve emitter locations



Lethiec, C.; *et al*. “Measurement of Three-Dimensional Dipole Orientation of a Single Fluorescent Nanoemitter by Emission Polarization Analysis.” Phys. Rev. X 2014, 4 (2), 021037.

Wide-field imaging setup (fixed polarization angles)

- High throughput & intrinsic drift correction
- Super-resolves emitter locations
- Orientation information from intensity distribution into 4 polarization channels

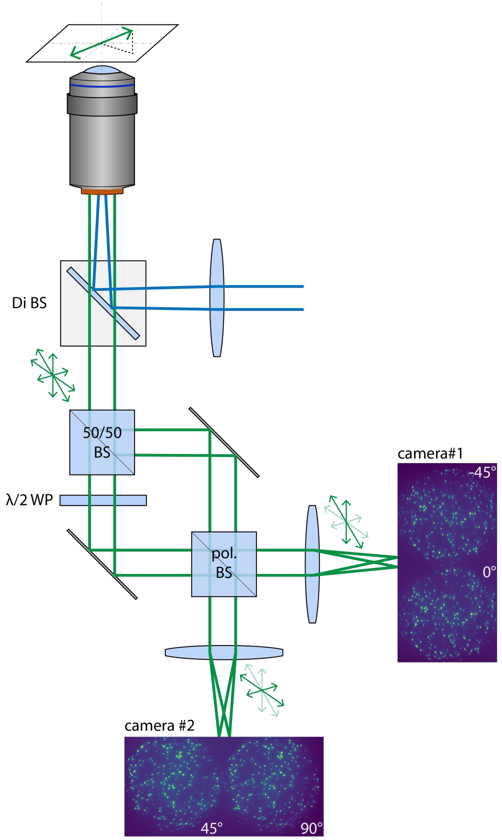


Polarization Imaging for Orientation Measurement

Super-resolved orientation

4 images

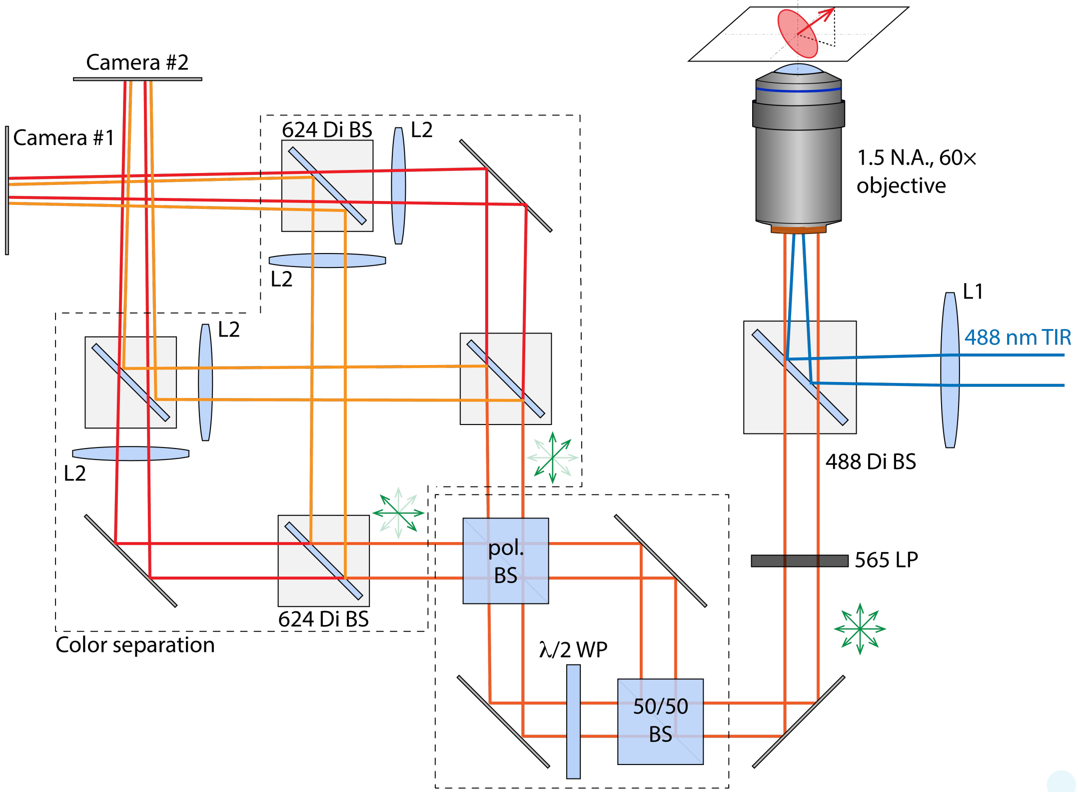
Calibration corrects for optical path efficiency differences

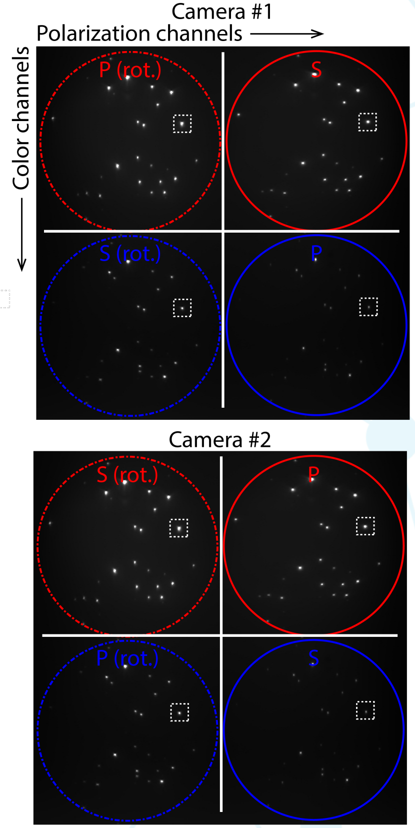


Super-resolved orientation + spectral

8 images

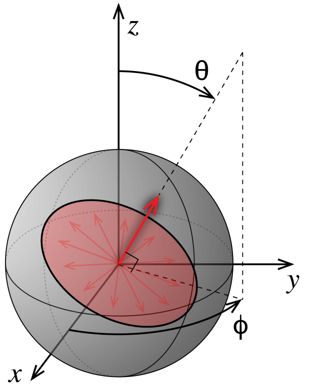
Calibration also considerations of polarization responses of dichroic mirrors



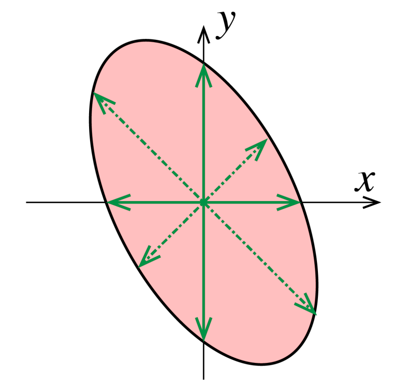


Ryan, D. P. *et al.* Quantum dot clusters visualized by polarization- and wavelength-resolved nanoscopy. *In prep.*

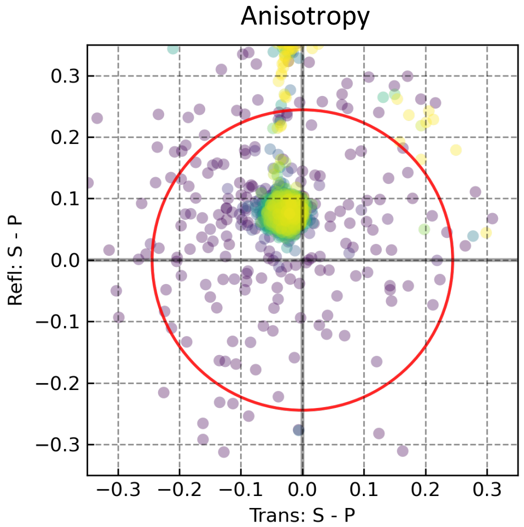
Orientation Imaging



2D dipole



Back focal plane projection

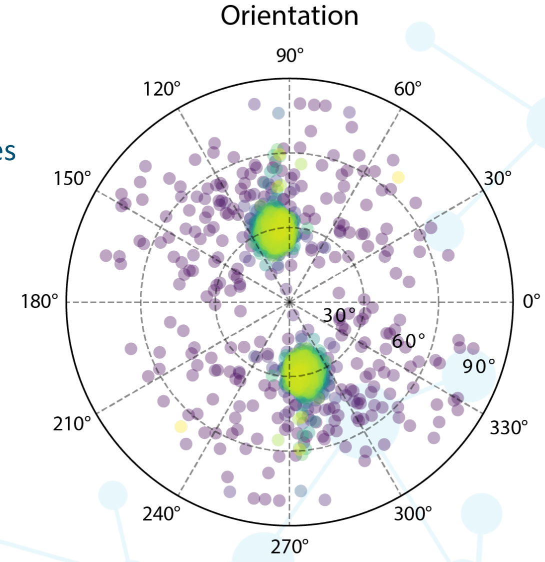


Anisotropy → Orientation angles

Intensity anisotropy between orthogonal polarization pairs measures the shape of the projected ellipse.

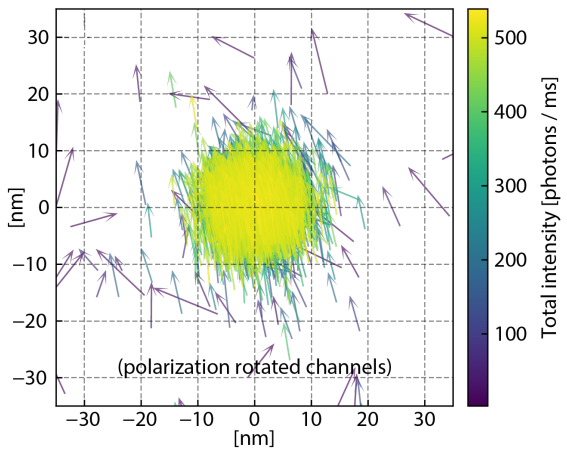
The orientation of a NP also requires an appropriate model of imaging system to determine the polar angle θ.

The azimuthal angle ϕ is two-fold degenerate.

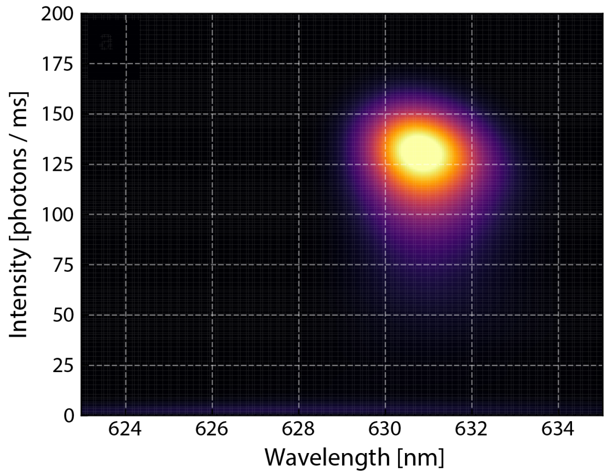


Orientation of a Single NP

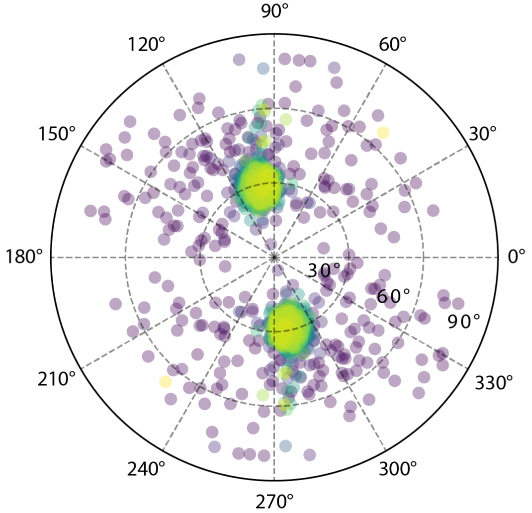
Super-resolution localization



Spectral-intensity distribution



Orientation

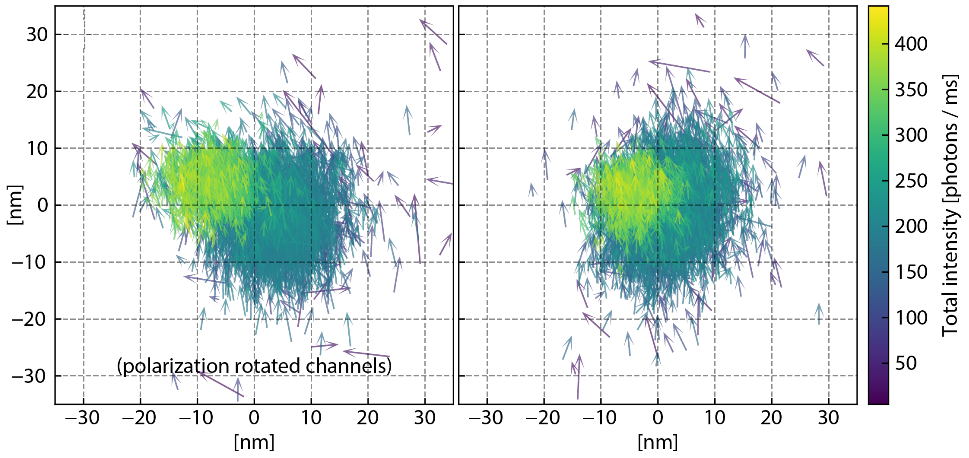


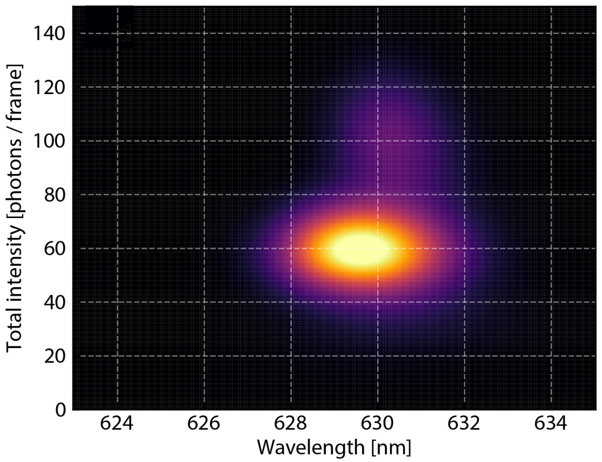
Isolated NPs localize to a single position.

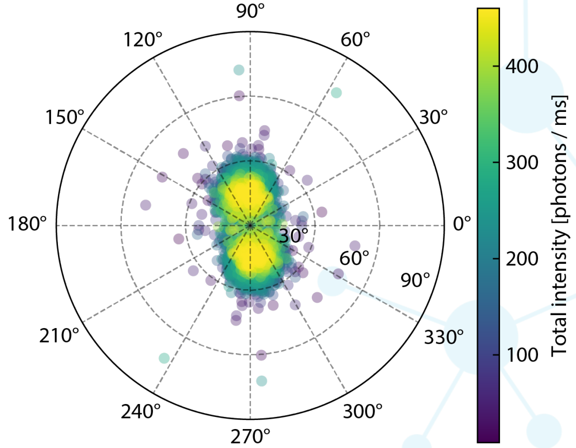
A single NP has a well-defined wavelength at a given intensity (bright state).

Ryan, D. P. *et al.* Quantum dot clusters visualized by polarization- and wavelength-resolved nanoscopy. *In prep*.

Orientation of a Small NP Cluster







With imaging configuration, each color/polarization channel generates a super-resolved image.

Because of PSF asymmetry, localization information from orthogonal pairs of polarization channels are required to generate a single super-resolution image.

Super-resolved images from the final two channel pairs produce similar shapes.

Spectral-intensity distribution follows energy transfer model: highest emission is from longer wavelength NPs and lower intensity donor emission is shorter wavelength.

Orientation signature indicates a single orientation.

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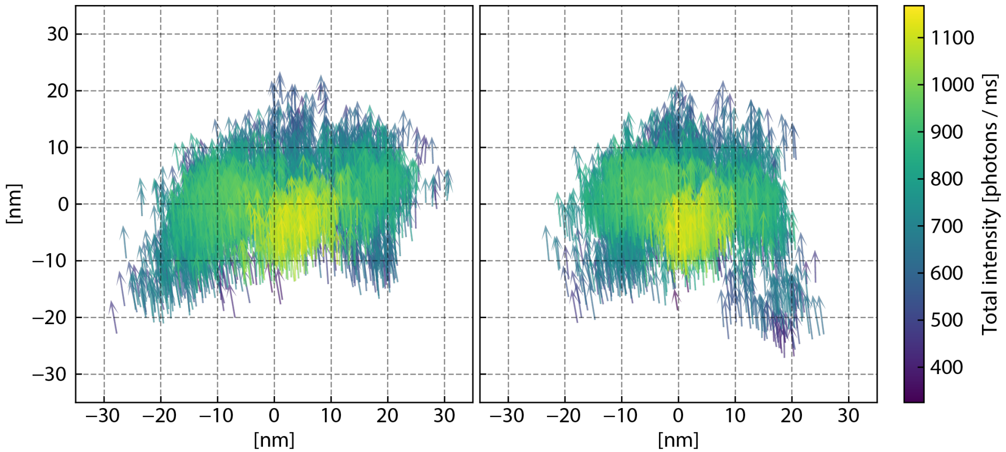
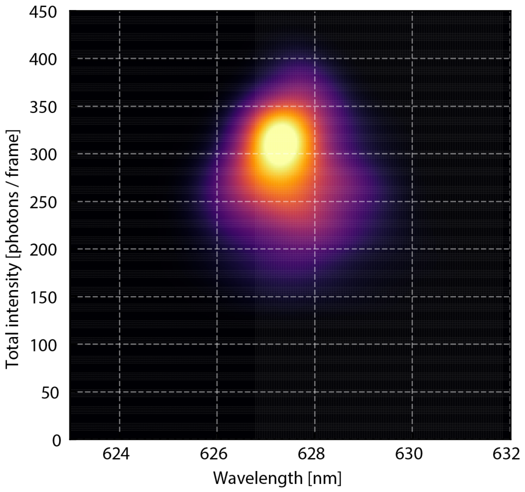
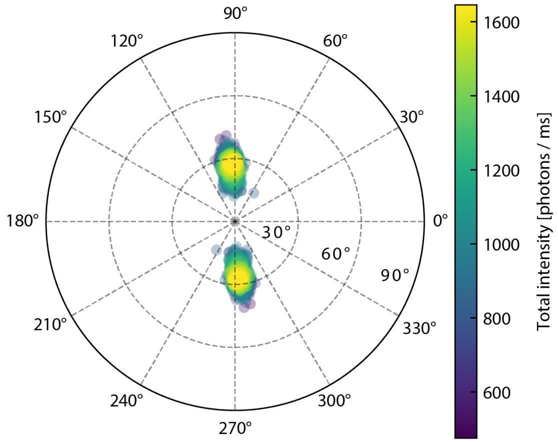
Orientation of a Large NP Cluster

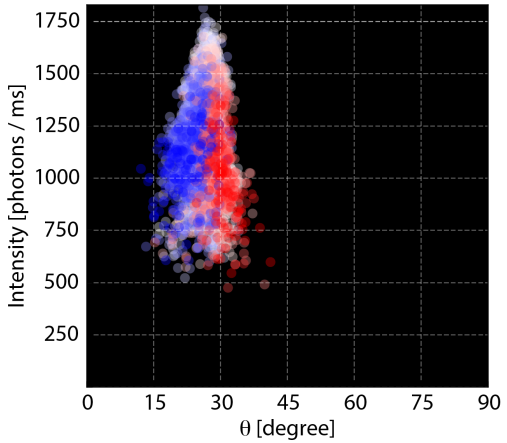




This larger NP cluster shows structural features, but a common alignment among the NPs, indicating oriented attachment.

The spectral signature of larger NP clusters tends to not exhibit the energy transfer relationship between wavelength and intensity.





The mild orientation variation is only present in the polar angle θ.

Color coding (blue/red) the orientation relative to the mean emission wavelength shows shorter wavelength emission originates from NPs with small tilt angles.

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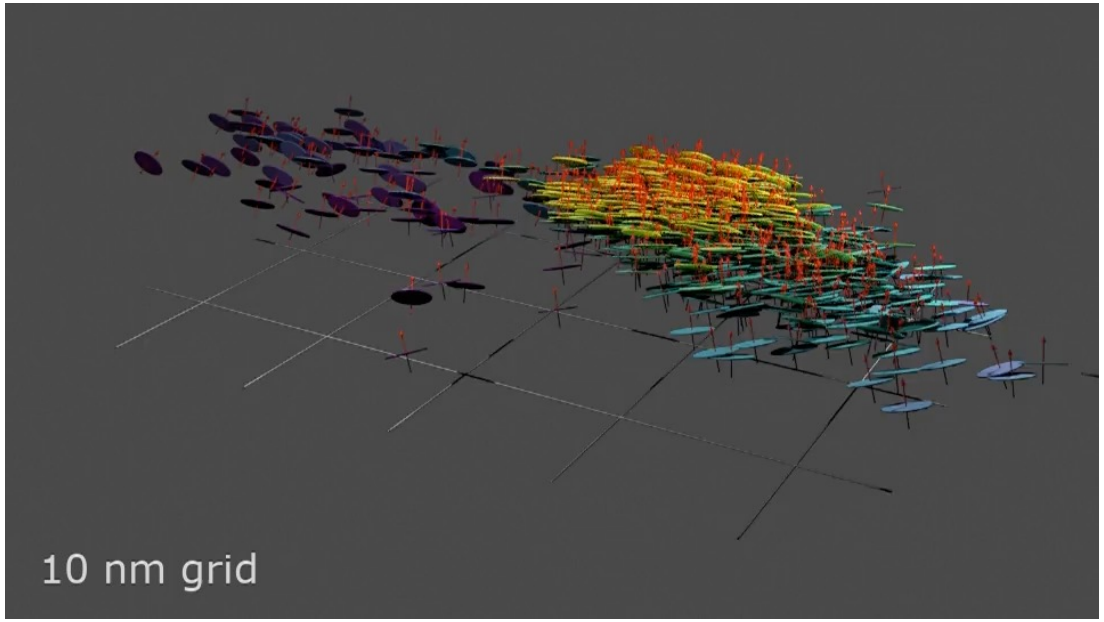
Conclusions



- Demonstrated orientation imaging using a wide-field polarization microscope.
- NP clusters have a narrow distribution of orientations, indicating particle alignment within cluster.

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